

CLAIMS

What is claimed is:

1. A perfluoropolyether comprising perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and a 1,2-bis(perfluoromethyl)ethylene diradical, $-\text{CF}(\text{CF}_3)\text{CF}(\text{CF}_3)-$, is absent in the molecule of said perfluoropolyether.
2. A perfluoropolyether according to claim 1 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.
3. A perfluoropolyether according to claim 1 wherein said perfluoropolyether has the formula of $\text{C}_r\text{F}_{(2r+1)}-\text{A}-\text{C}_r\text{F}_{(2r+1)}$; each r is independently 3 to 6; if $r = 3$, both end groups $\text{C}_r\text{F}_{(2r+1)}$ must be a propyl radical; A is selected from the group consisting of $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_w$, $\text{O}-(\text{C}_2\text{F}_4-\text{O})_w$, $\text{O}-(\text{C}_2\text{F}_4-\text{O})_x(\text{C}_3\text{F}_6-\text{O})_y$, $\text{O}-(\text{CF}_2\text{CF}_2\text{CF}_2-\text{O})_w$, $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_x(\text{CF}_2\text{CF}_2-\text{O})_y-(\text{CF}_2-\text{O})_z$, and combinations of two or more thereof; w is 4 to 100; and x , y , and z are each independently 1 to 100.
4. A composition comprising a perfluoropolyether, which comprises perfluoroalkyl radical end groups wherein said radical has at least 3 carbon atoms per radical and is substantially free of perfluoromethyl and perfluoroethyl, and 1,2-bis(perfluoromethyl)ethylene diradical, $-\text{CF}(\text{CF}_3)\text{CF}(\text{CF}_3)-$, is absent in the molecule of said perfluoropolyether.
5. A composition according to claim 4 wherein said perfluoroalkyl radical has 3 to 6 carbon atoms per radical.
6. A composition according to claim 4 wherein said perfluoropolyether has the formula of $\text{C}_r\text{F}_{(2r+1)}-\text{A}-\text{C}_r\text{F}_{(2r+1)}$; each r is independently 3 to 6; if $r = 3$, both end groups $\text{C}_r\text{F}_{(2r+1)}$ must be a propyl radical; A is selected from the group consisting of $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_w$, $\text{O}-(\text{C}_2\text{F}_4-\text{O})_w$, $\text{O}-(\text{C}_2\text{F}_4-\text{O})_x(\text{C}_3\text{F}_6-\text{O})_y$, $\text{O}-(\text{CF}_2\text{CF}_2\text{CF}_2-\text{O})_w$, $\text{O}-(\text{CF}(\text{CF}_3)\text{CF}_2-\text{O})_x(\text{CF}_2\text{CF}_2-\text{O})_y-(\text{CF}_2-\text{O})_z$, and combinations of two or more thereof; w is 4 to 100; and x , y , and z are each independently 1 to 100.

7. A composition according to claim 4 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

8. A composition according to claim 5 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

9. A composition according to claim 6 further comprising a thickener and said perfluoropolyether is present in said composition in the range of from about 0.1 to about 50 weight % based on said composition.

10. A composition according to claim 9 wherein said thickener is selected from the group consisting of poly(tetrafluoroethylene), fumed silica, and boron nitride, and combinations of two or more thereof.

11. A process for producing a perfluoropolyether comprising (1) contacting a reactant with a metal halide to produce an alkoxide wherein said reactant is selected from the group consisting of a perfluoro acid halide, a C₂ to C₄-substituted ethyl epoxide, a C₃+ fluoroketone, and combinations or two or more thereof; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to its corresponding alcohol; (5) converting said corresponding alcohol with a base to a salt; (6) contacting said salt with a C₃+ olefin or perfluoroalkene to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

12. A process according to claim 11 wherein said C₃+ olefin is a C₃-C₆ straight chain olefin, C₃-C₆ branched chain olefin, C₃-C₆ allyl halide, or combinations of two or more thereof.

13. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting

said salt with a C₃ or higher olefin to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

14. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting said salt with a C₃₊ branched fluoroalkene or a C₃₊ allyl halide to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

15. A process according to claim 11 wherein said process comprises (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

16. A process according to claim 11 wherein said process comprises (1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) contacting said ester with a Grignard reagent to produce a carbinol; and (5) dehydrating or fluorinating said carbinol.

17. A process according to claim 11 wherein said process comprises (1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a base to produce a salt; (6) contacting said salt with a C₃₊ olefin to produce a fluoropolyether; and (7) fluorinating said fluoropolyether.

18. A process according to claim 11 wherein said process comprises
(1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide;
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane
to produce a second acid halide; (3) esterifying said second acid halide to an ester;
5 (4) reducing said ester to its corresponding alcohol; (5) converting said
corresponding alcohol with a base to a salt; (6) contacting said salt with a C₃₊
fluoroalkene to produce a fluoropolyether; and (7) fluorinating said
fluoropolyether.

19. A process according to claim 11 wherein said process comprises
10 (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with
a metal halide to produce an alkoxide; (2) contacting said alkoxide with
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;
(3) contacting said second acid halide with a metal iodide to produce a second
iodide; (4) fluorinating said second iodide.

20. A process according to claim 11 wherein said process comprises
15 (1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide;
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane
to produce an acid halide; (3) contacting said acid halide with a metal iodide to
produce a second iodide; (4) fluorinating said second iodide.

21. A process according to claim 11 wherein said process comprises
20 (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with
a metal halide to produce an alkoxide; (2) contacting said alkoxide with
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;
(3) contacting said second acid halide with a metal iodide to produce a second
25 iodide; (4) contacting said second iodide with an olefin to produce a third iodide;
and (5) fluorinating said third iodide.

22. A process according to claim 11 wherein said process comprises
(1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide;
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane
30 to produce an acid halide; (3) contacting said acid halide with a metal iodide to
produce a second iodide; (4) contacting said second iodide with an olefin to
produce a third iodide; and (5) fluorinating said third iodide.

23. A process according to claim 11 wherein said process comprises
(1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with
a metal halide to produce an alkoxide; (2) contacting said alkoxide with
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;
5 (3) contacting said second acid halide with a metal iodide to produce a second
iodide; (4) contacting said second iodide with an olefin to produce a third iodide;
(5) dehydrohalogenating said third iodide to give a second olefin; and (6)
fluorinating said second olefin.

24. A process according to claim 11 wherein said process comprises
10 (1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide;
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane
to produce an acid halide; (3) contacting said acid halide with a metal iodide to
produce a second iodide; (4) contacting said second iodide with an olefin to
produce a third iodide; (5) dehydrohalogenating said third iodide to give a second
15 olefin; and (6) fluorinating said second olefin.

25. A process according to claim 11 wherein said process comprises
fluorinating a fluoropolyether having alkyl radical end groups; said radical has at
least 3 carbon atoms per radical and is substantially free of methyl and ethyl; and
a 1,2-bis(methyl)ethylene diradical, -CH(CH₃)CH(CH₃)-, is absent in the
20 molecule of said fluoropolyether.

26. A process according to claim 25 wherein said process is carried out
in the presence of a mixture comprising an inert solvent and a hydrogen fluoride
scavenger.

27. A process according to claim 11 wherein said process comprises
25 (1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with
a metal halide to produce an alkoxide; (2) contacting said alkoxide with
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;
(3) contacting said second acid halide with a metal iodide to produce a second
iodide; (4) replacing the iodine radicals of said second iodide with hydrogen
30 radicals to produce a fluoropolyether containing hydrogen radicals; and (5)
fluorinating said fluoropolyether.

28. A process according to claim 11 wherein said process comprises
(1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide;
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane
to produce an acid halide; (3) contacting said acid halide with a metal iodide to
5 produce a second iodide; (4) replacing the iodine radicals of said second iodide
with hydrogen radicals to produce a fluoropolyether containing hydrogen radicals;
and (5) fluorinating said fluoropolyether.

29. A process according to claim 11 wherein said process comprises
(1) contacting a perfluoro acid halide or a C₂ to C₄-substituted ethyl epoxide with
10 a metal halide to produce an alkoxide; (2) contacting said alkoxide with
hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide;
(3) contacting said second acid halide with a metal iodide to produce a second
iodide; (4) contacting said second iodide with an olefin to produce a third iodide;
(5) replacing the iodine radicals of said second iodide with hydrogen radicals to
15 produce a fluoropolyether containing hydrogen radicals; and (6) fluorinating said
fluoropolyether.

30. A process according to claim 11 wherein said process comprises
(1) contacting a C₃ to C₆ fluoroketone with a metal halide to produce an alkoxide;
(2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane
20 to produce an acid halide; (3) contacting said acid halide with a metal iodide to
produce a second iodide; (4) contacting said second iodide with an olefin to
produce a third iodide; (5) replacing the iodine radicals of said second iodide with
hydrogen radicals to produce a fluoropolyether containing hydrogen radicals; and
(6) fluorinating said fluoropolyether.

31. A process according to claim 11 wherein said process comprises
(1) contacting a perfluoro acid halide, a C₃ to C₆ fluoroketone, or a C₂ to C₄-
substituted ethyl epoxide with a metal halide to produce an alkoxide; (2)
contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to
produce a second acid halide; (3) esterifying said second acid halide to an ester;
30 (4) reducing said ester to an alcohol; (5) contacting said alcohol with sulfur
tetrafluoride or derivative thereof to convert the OH groups of said alcohol to

fluorine radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

32. A process according to claim 11 wherein said process comprises
- (1) contacting a perfluoro acid halide, a C₃ to C₆ fluoroketone, or a C₂ to C₄-substituted ethyl epoxide with a metal halide to produce an alkoxide; (2) contacting said alkoxide with hexafluoropropylene oxide or tetrafluorooxetane to produce a second acid halide; (3) esterifying said second acid halide to an ester; (4) reducing said ester to an alcohol; (5) contacting said alcohol with a phosphorus pentahalide or derivative thereof to convert the OH groups of said alcohol to halide radicals thereby producing a fluoropolyether; and (6) fluorinating said fluoropolyether.

33. A process according to claim 11 wherein said process comprises
- (1) contacting a fluorotertiary alkoxy-containing compound with a first fluoropolyether to produce a second fluoropolyether and optionally (2) fluorinating said second fluoropolyether wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol or a perfluoro-t-butyl hypofluorite; said first fluoropolyether has (i) a starting C₃-C₆ segment or R_f⁸(R_f⁹)CFO segment and (ii) a -A-O-C(CF₃)=CF₂ or a -A-O-C(CF₃)=CHF intermediate end group; R_f⁸ is C_jF_(2j+1); R_f⁹ is C_kF_(2k+1); j and k are each ≥ 1; (j + k) ≤ 5; and A is selected from the group consisting of O-(CF(CF₃)CF₂-O)_w, O-(CF₂-O)_x(CF₂CF₂-O)_y, O-(C₂F₄-O)_x, O-(C₂F₄-O)_x(C₃F₆-O)_y, O-(CF(CF₃)CF₂-O)_x(CF₂-O)_y, O(CF₂CF₂CF₂O)_w, O-(CF(CF₃)CF₂-O)_x(CF₂CF₂-O)_y-(CF₂-O)_z, and combinations of two or more thereof.

34. A process according to claim 33 wherein said fluorotertiary alkoxy-containing compound is a salt of a fluorotertiary alcohol.

35. A process according to claim 33 wherein said fluorotertiary alkoxy-containing compound is a perfluoro-t-butyl hypofluorite.